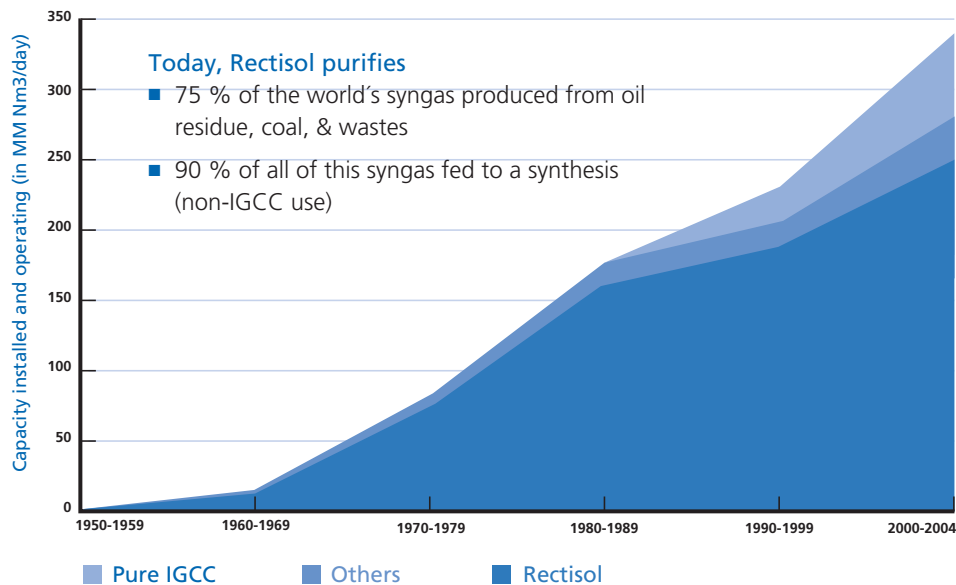


The Rectisol® Process

Lurgi's leading technology for purification
and conditioning of synthesis gas



After 50 years still unrivalled in the purification of syngas (Diagram derived from the SFA Pacific World-wide Gasification Database 2004)

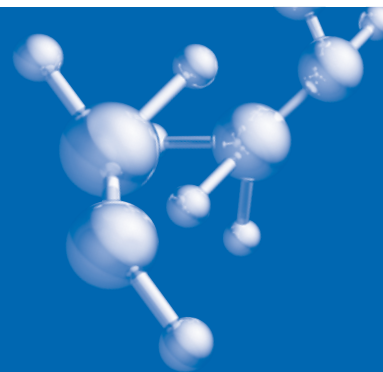
History

The first Rectisol installation was started up in Sasolburg, Republic of South Africa, in 1955. In the following decades Rectisol paved the way for huge-scale ammonia and Fischer Tropsch Synthesis. In the 1970s and 80s, oil residue gasification proved to be another field of application. The impressive success of this technology is visualized above.

Nowadays, more than half a century later, Rectisol is still unique reaching synthesis gas quality in one single process. Meanwhile, a bunch of alternative technologies appeared on the market for the "simple" removal of sulfur compounds and CO₂. However, Rectisol is still the only process taking care of all other raw gas contaminants specific for coal and oil gasification, sometimes only present in parts per billion (ppB) in the raw syngas.

Because of this, the comeback of the coal gasification technology experienced in the first decade of the millennium comes along with an impressive boost in the track record of Rectisol plants: Nearly each of the coal gasification units for production of ammonia, methanol, hydrogen or synfuels is or will be equipped with a Rectisol gas purification system. This will result in another sharp increase in the curve depicted above when the plants are in operation.

In the new millennium, the purification of syngas produced by gasification of heavy oil residue from recovery from oil shale or oil sands are a new field of application adding to the "classics", coal, lignite and refinery residue gasification.



Performance

The principal useful components of a raw syngas gas produced by heavy oil or coal gasification are H_2 and CO . Dependent on the feedstock and type of gasification process this raw gas can contain 3–40% CO_2 as well as smaller fractions of CH_4 , H_2O , N_2 and Ar. Trace contaminants present may be H_2S , COS , HCN , NH_3 , nickel and iron carbonyls, gum formers, CS_2 , mercaptans, naphthalene, thiophenes, organic sulfides, and higher hydrocarbons. In order to obtain the gas quality needed for its usage as a feedstock for a synthesis, as e.g. ammonia synthesis, methanol synthesis, Fischer Tropsch Synthesis, oxo-alcohol synthesis or simply as hydrogen product, reduction gas or town gas, these impurities must be removed. This especially holds true for the trace contaminants which usually have to be eradicated.

Typical purity requirements for synthesis gas:

- | | |
|----------------|---|
| ■ Total sulfur | less than 0.1 ppm by volume |
| ■ CO_2 | 2 ppm to 3% by volume
depending on the type of synthesis |

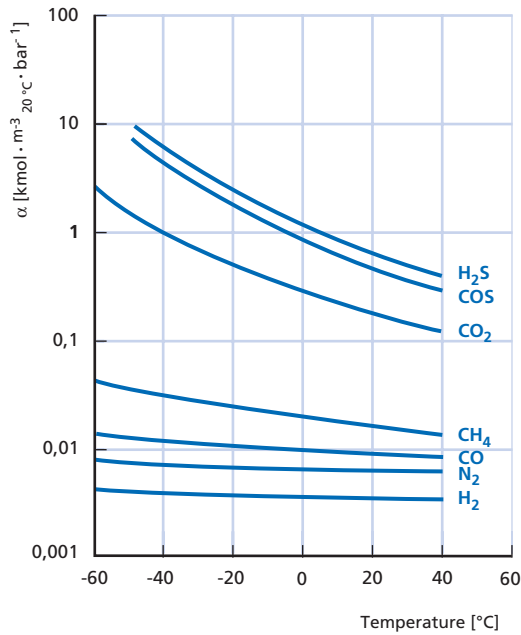
Sulfur compounds, HCN and NH_3 should be discharged in a stream as concentrated as possible so as to improve the economics of subsequent treatment. The CO_2 must be sufficiently clean to allow it to be discharged directly to atmosphere or even used as a product.

The CO_2 separated from the gas can be a mixture with nitrogen when it is vented to the atmosphere. If the CO_2 is used as a feedstock for another process (e.g. in a urea synthesis or for production of food grade CO_2) the CO_2 has to be partially or completely recovered as a highly concentrated, pure and dry product stream. The allowable residual H_2S content for both cases typically varies in a range of 5–25 ppmV.

To summarize, the following functions have to be fulfilled by the gas purification system:

- Trace contaminant removal
- Deep de-sulfurization
- Drying
- Bulk CO_2 removal
- CO_2 purification
- Acid gas enrichment

Where other approaches may end up with up to six separate processes, the Rectisol technology provides an excellent option to stick with only one integrated technology and plant, yielding excellent results with respect to performance and reliability. In order to judge correctly on complexity, investment costs and consumption figures for Rectisol vs. alternative schemes, battery limits have to be set correctly: For example Rectisol absorbs also COS so that a separate COS hydrolysis process upstream of the gas wash is not needed.



Absorption coefficient α of various gases in methanol (partial pressure: 1 bar)

Process Principle

Rectisol has been successfully applied for purifying syngas produced by:

- Sasol/Lurgi Fixed Bed Dry Bottom Coal and Lignite Gasification
- Lurgi British Gas BGL Coal gasification
- Lurgi MPG Heavy Oil Gasification
- Shell Oil Gasification
- Shell Coal Gasification
- GE (former Texaco) Oil & TAR Gasification
- GE (former Texaco) Petcoke Gasification
- Reformed gas from natural gas reformers

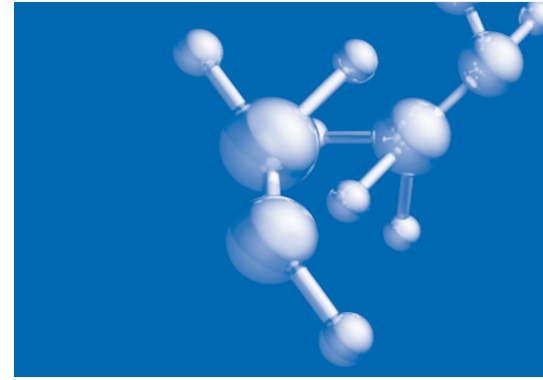
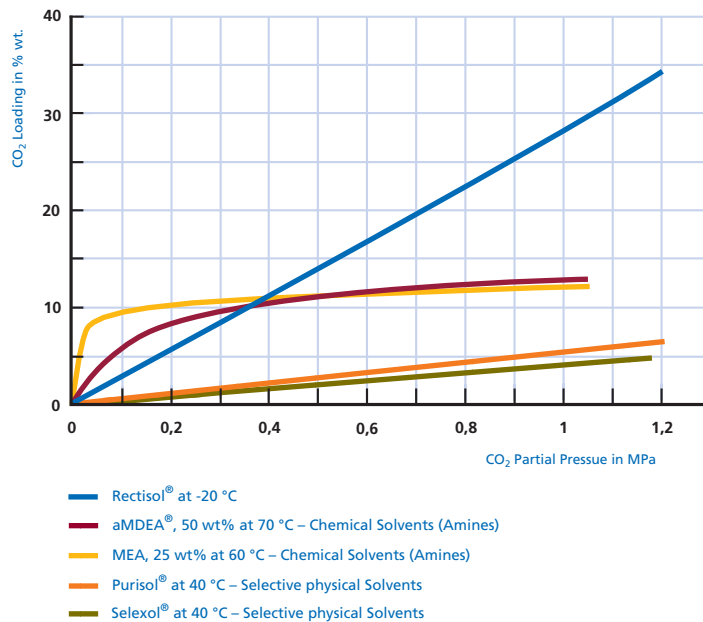
Rectisol uses refrigerated methanol as the solvent for physical absorption.

The undesired components of the raw gas, such as CO₂, H₂S, COS and the remaining sulfur compounds, HCN, NH₃, as well as nickel and iron carbonyls are physically absorbed from the raw gas by the solvent. These components are then desorbed by reducing the pressure of the solvent, stripping and, if required, reboiling the solvent. The absorbed higher hydrocarbons are recovered in an additional extraction stage, if necessary.

The solubility of the different components to be removed varies considerably. This also applies to H₂S and CO₂ and allows selective removal of these components.

The solubility data of the various gases in methanol are illustrated above.

Since the solubility data of H₂S and the organic sulfur compounds are appreciably higher than that of CO₂, the H₂S concentration in the Claus gas can be increased to acceptable levels even if the H₂S to CO₂ ratio in the raw gas is unfavorable.

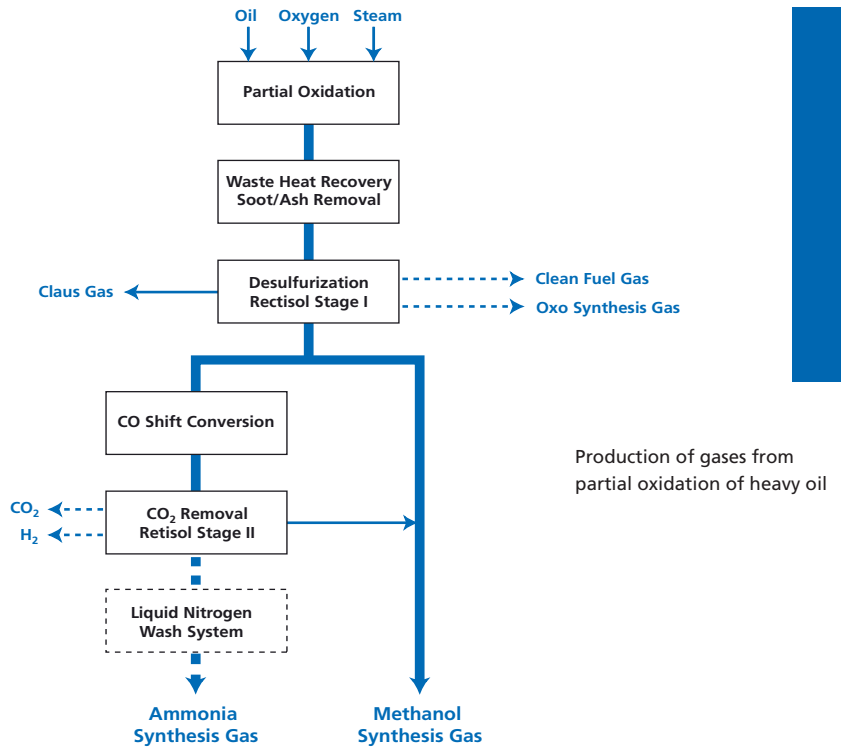


CO₂ Bulk Removal capacity of different types of solvents

The solubility of the trace components HCN, NH₃ and sulfur compounds like mercaptans are much higher than those of H₂S. This makes it possible to remove them separately using a very small solvent rate in a prewash stage. The rich methanol from this prewash stage is regenerated by integrating this loop into the H₂S hot regeneration system so that these trace components are routed directly to the Claus gas. Rectisol also provides excellent performance in separating big amounts of CO₂ from the gas. At CO₂ partial pressures – due to high concentration in the feed gas and/or due to high gasification pressure – the absorption capacity of low temperature methanol exceeds the one of each alternative solvent.

The process is extremely flexible, a feature which allows it to be tailored to a large number of different individual applications. The block flow diagram shows one possible arrangement starting with the gasification of heavy oil using the Lurgi Multi Purpose Gasification Process (MPG). The example focuses on the production of methanol. However, additional possibilities for other products are indicated by dotted lines.

On page 8, we show a simplified process flow diagram for this scheme. In this example, the gas train is equipped with a clean gas shift, integrated in the Rectisol system. Schemes where a raw gas shift is installed upstream of the Rectisol unit are also possible and demonstrated manifoldly.



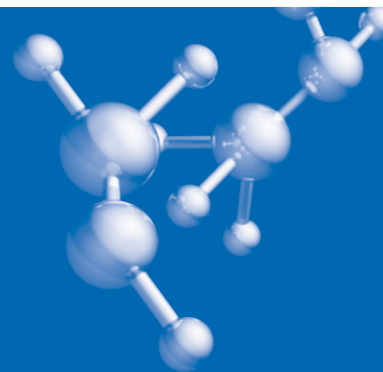
Process Description

The raw gas entering the plant is cooled. The trace components like HCN and NH₃ are removed in the prewash stage with cold methanol.

Thereafter, the sulfur is removed from the gas using CO₂-laden solvent to a residual sulfur content of below 0.1 ppm. The solvent from the H₂S absorber is regenerated first by flashing at medium pressure to recover the useful gases (H₂ and CO) and then by heating to boiling temperature and stripping with methanol vapor.

In cases where there is sufficient H₂S in the raw gas, hot regeneration produces a Claus gas with adequate H₂S content for further treatment without any special measures needing to be taken. Where the H₂S content of the raw gas is lower or the CO₂ content higher an additional stage, stripping and reabsorption, must be provided.

The portion of the clean gas which has been shifted in the CO shift conversion unit has a typical CO₂ content of 33%. This gas re-enters the Rectisol unit, is cooled, and CO₂ is removed in a two-stage CO₂ absorber. In the lower section, the CO₂ content of the gas is reduced to about 5% using flash-regenerated methanol. The remaining CO₂ is removed using hot regenerated, cold methanol in the upper section so that about 3% CO₂ is contained in the synthesis gas.



The flashed CO₂ is free of sulfur and can be discharged directly to atmosphere. Under certain circumstances a water wash system may be necessary to further reduce the residual content of methanol in the CO₂ for environmental reasons. The refrigeration balance of the system is maintained by the refrigeration plant.

As the raw gas usually is saturated with water, a small portion of water is fed to the plant, which is also completely absorbed by the solvent. The water content of the solvent is kept at the desirable low level by continuously distilling a small side stream of the solvent circulation in a methanol/water distillation column which due to simplicity is not depicted in the schemes. An important feature of Rectisol is that this water leaves the distillation as the bottom product, carrying heavy boiling trace contaminants, salts, other trace contaminants and/or even Ni and Fe sulfides formed in

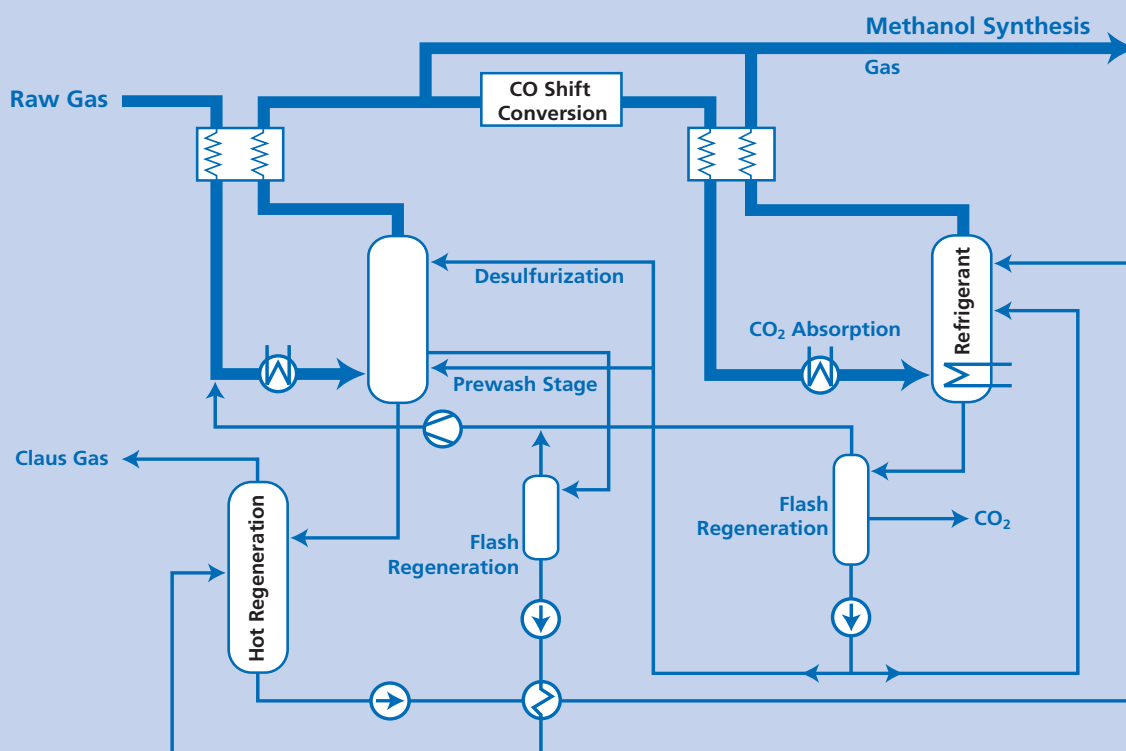
through decomposition of the carbonyls, if present in the raw gas. Nevertheless, as the concentration of such components is small, the water can be routed directly to a biological water treatment for work-up.

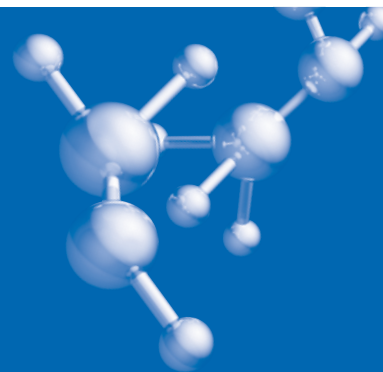
Utility Consumption (typical)

Reference is made to a 2,000 metric tons per day methanol plant.

■ Electric power (without refrigeration unit)	1,600 kW
■ Low pressure steam	5,500 kg/h
■ Cooling water (temp. difference: 10 K)	130 m ³ /h
■ Refrigeration duty (boiling temperature: -31 °C)	4,200 kW _{th}

Selective desulfurization and CO₂ removal to produce methanol synthesis gas





Other applications

This arrangement can be modified for production of pure gas streams fulfilling other product requirements. This may be mainly with respect to the stoichiometric ratio between H_2 and CO in the product gas, required by type of the downstream synthesis process, or with respect to purity requirements for certain components. In principle, one single Rectisol scheme could provide the whole indicated product range simultaneously, although usually only one or two of the products are needed.

Clean Coal Technologies & Carbon Capture & Storage

With the beginning of the new millenium, the world experiences a revival of coal as the raw material for the production of chemicals, petrochemicals and even synthetic natural gas (SNG). Clean coal technology (CCT) allow the processing of coal in an environmentally friendly manner, thus challenging the general perception as coal being the source of "dirty" power.

As a key consequence from the Kyoto protocol, CO_2 emission reduction will be a vital issue – talking about coal, Carbon Capture and Storage (CCS) is the key to this. CCS has the potential to settle the controversy caused by the trend back to coal on one hand and the postulation for mitigation of the global CO_2 emissions postulated in the Kyoto protocol on the other hand.

Rectisol is a key technology for both CCT as well as CCS: The most promising route for CO_2 emission free production of electricity from coal, lignite, oil residue, biomass and wastes is a Zero Emission Integrated Gasification Combined Cycle (ZE IGCC). In a ZE IGCC, CO_2 can be separated in an elegant manner and prepared for underground storage easily, such that the efficiency loss can be kept low.

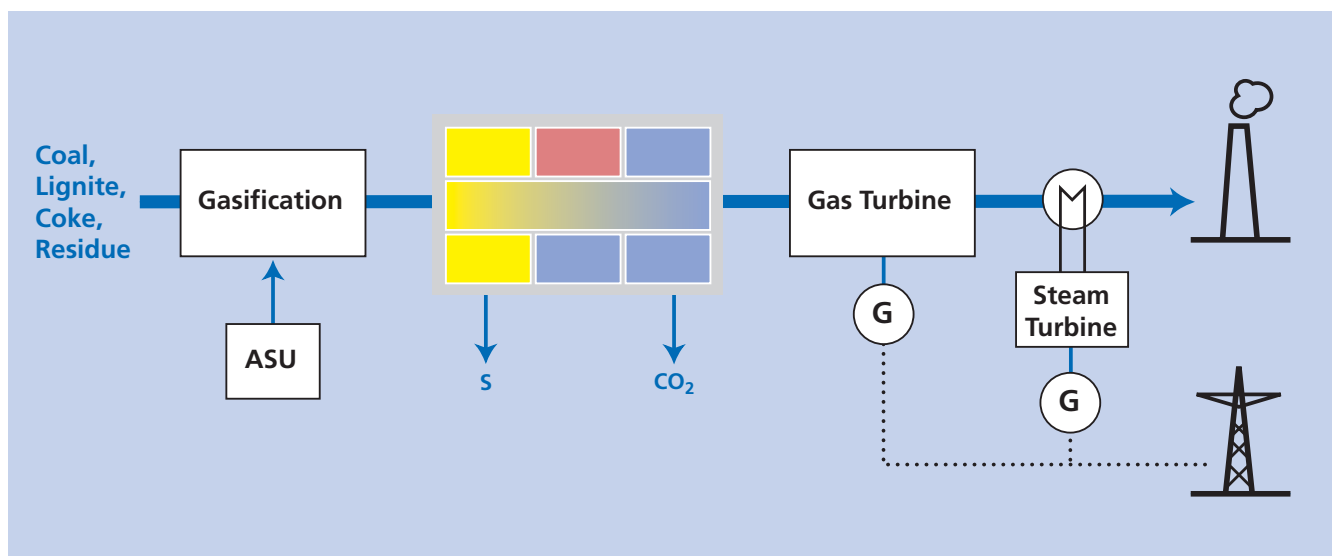
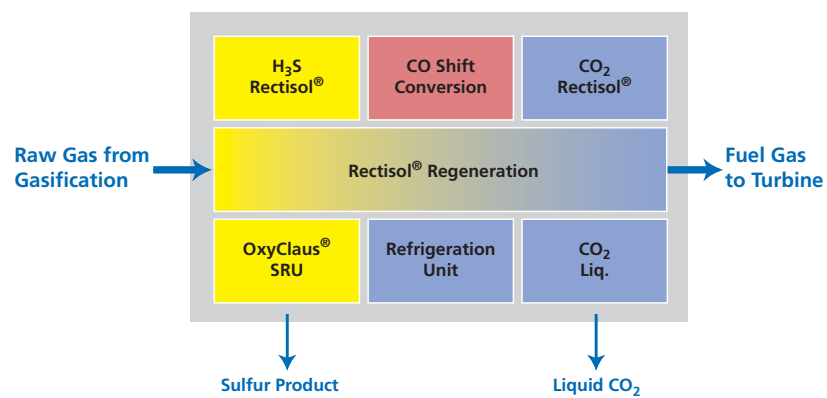
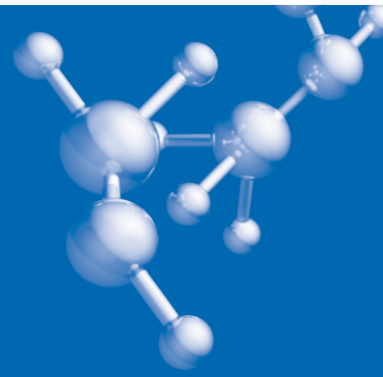
In the COORIVA project, founded by the BMWA, a consortium of leading German utilities and engineering companies develops the German ZE IGCC, fuelled with lignite or hard coal. It will enable us to generate CO_2 emission-free power from coal in a very efficient and environmentally friendly manner. Contributing its excellent capabilities with respect to trace contaminants, bulk CO_2 removal and overall reliability, Lurgi Rectisol is the key technology in the "Fuel Gas Conditioning", provided by Lurgi, allowing to produce the CO_2 in the purity and quality needed for safe storage or other usage, as for example Enhanced Oil Recovery (EOR). The Lurgi OxyClaus® sulfur plant is integrated in a way with the Rectisol system that no further source of emission exists apart from the nearly CO_2 -free exhaust gas of the power island. Aside of the hydrogen fuel gas fed to the gas turbine and the pure, dry, liquid CO_2 produced, the only co-product is saleable "bright yellow" sulfur.

The emission-free gas conditioning concept of the Cooriva ZE IGCC can be easily transferred to every coal or oil residue gasification based project, whatever the usage of the purified syngas is. Thus the ZE IGCC is only one example for a whole family of Zero Emission Syngas Technologies (ZEST), taking care of the energy and product demands of today as well as of the climate of tomorrow.

Technological Highlights of Rectisol

- Removal of all impurities and trace contaminants in one single absorption process
- Ultra-pure product gas: e.g. total sulfur <0.1 ppmV, CO₂ <2 ppmV
- Tailor-made stoichiometrics for any kind of synthesis either with raw gas shift or integrated clean gas shift
- Multi-product application possible in one single unit, e.g. methanol-syngas plus ammonia syngas plus hydrogen plus IGCC fuelgas
- All gaseous products are completely dry
- Thermal regeneration usually only for a smaller portion of the solvent, cheap flash regeneration and/or nitrogen stripping for the rest. Acid gas enrichment: A suitable Claus gas can be produced even with a CO₂/H₂S ratio up to 700 in the raw feed gas
- A pure CO₂ product stream, ready for Enhanced Oil Recovery, underground storage or chemical usage can be produced
- Inexpensive, thermally and chemically stable solvent, available worldwide anywhere.

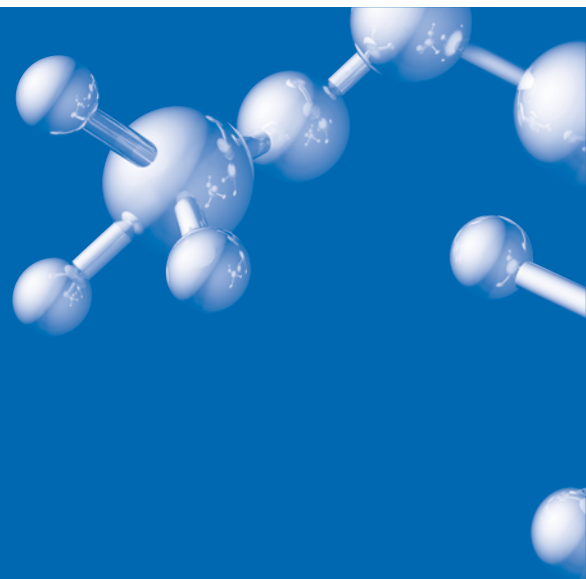
No degradation, no corrosion, no disposal problems.



Zero Emission IGCC with integrated Rectisol based "fuel gas conditioning"

Lurgi is a leading technology company operating worldwide in the fields of process engineering and plant contracting. The strength of Lurgi lies in innovative technologies of the future focusing on customized solutions for growth markets. The technological leadership is based on proprietary technologies and exclusively licenced technologies in the areas gas-to-petrochemical products via synthesis gas or methanol and synthetic fuels, petrochemicals, refinery technology and polymer industry as well as renewable resources/food. Lurgi is a company of Air Liquide Group.

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